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(54) Method of Treating Nitrite-
containing Waste Water

(57) The waste water has its pH
adjusted to 2 to 5 (using, for example,
HCl, H₂SO₄ or HNO₃) and then nitrite
ions in the waste water are oxidised to
nitrate ions by means of hydrogen
peroxide.

The oxidation end-point is
preferably determined titrimetrically
using an oxidation-reduction
potentiometer, addition of hydrogen
peroxide until the end-point being
controlled automatically by a suitable
electrical circuit.

After the oxidation, the solution is
neutralised and then discharged.

The drawings originally filed were
informal and the print here
reproduced is taken from a later
filed formal copy.

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FIG. 1

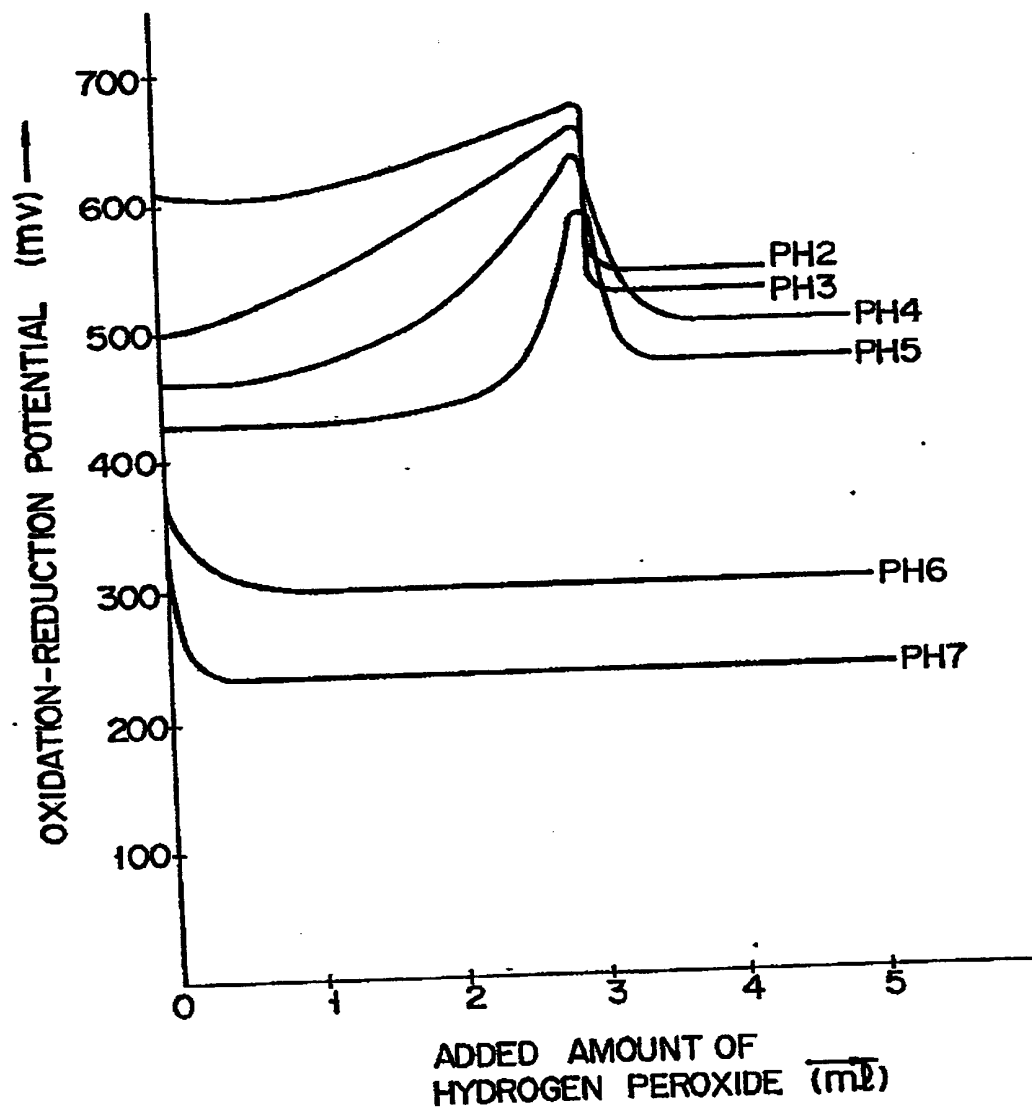


FIG. 2

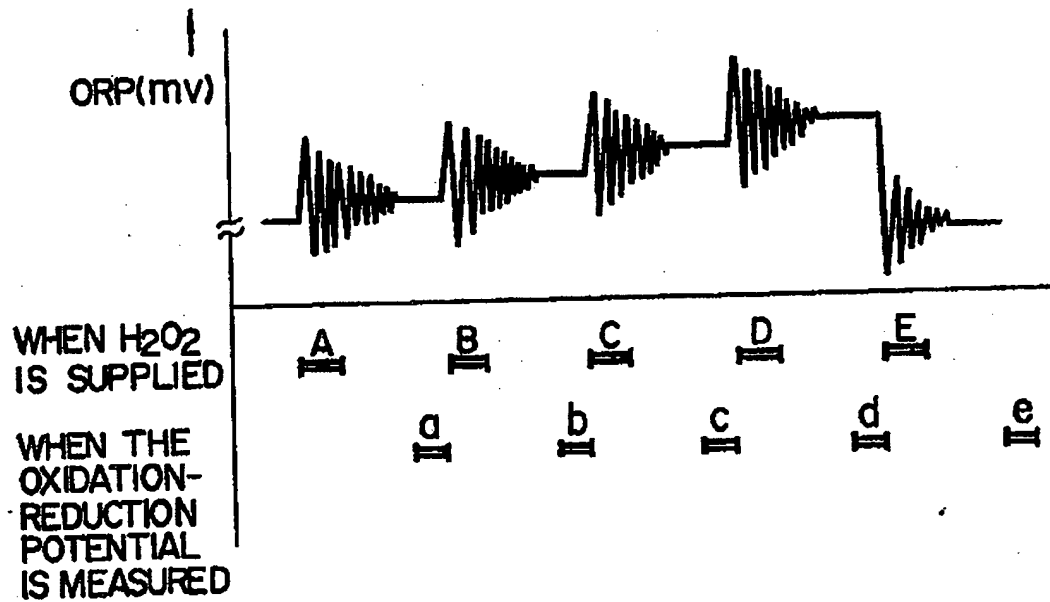
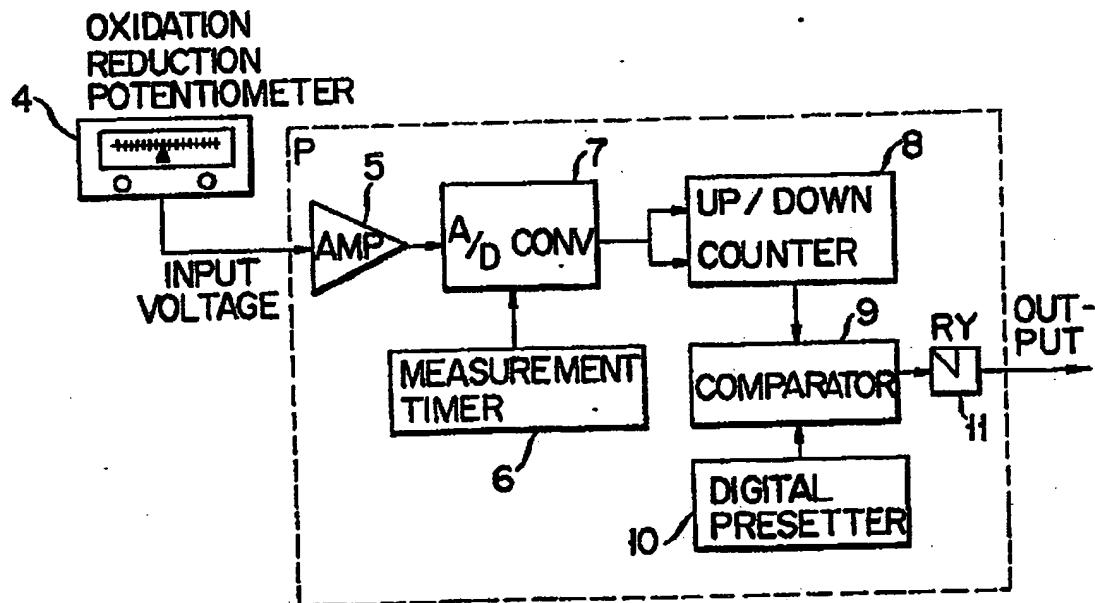


FIG. 3



SPECIFICATION

Method of Treating Nitrite-containing Waste Water

The present invention is concerned with a method of treating waste water containing dissolved nitrite ions prior to discharge of the water to the environment.

5 Waste water containing dissolved nitrite ions is produced in many processes, such as nitration, nitric acid oxidation and nitrogen oxide-absorbing processes, as well as processes in which a molten salt bath comprising a nitrate and a nitrite is used. Such a molten salt bath is used, for example, in the heat treatment of metals, the processing of soft polyvinyl chloride and the vulcanization of rubber products. Where, for example, a metal material is treated in direct contact with the molten salt mixture, then it is necessary to wash the treated material with clear water, such that a small amount of nitrite is 10 unavoidably carried into the waste water.

Nitrite ions present in waste water cause the water to have a high chemical oxygen demand (COD), that is, the amount of oxygen, expressed in p.p.m., required to fully oxidise materials present in the waste water. The COD should be reduced before the waste water is discharged to the environment 15 and it has been proposed to oxidise the nitrite ions to nitrate ions, for example, using a heavy metal oxidant or a photo-oxidation process. The use of a heavy metal oxidant is disadvantageous as such materials are themselves pollutants, while the use of a photo-oxidation process is not satisfactory as the efficiency of the oxidation is too low for commercial purposes.

We have now developed an improved method of oxidising nitrite ions present in waste water. 20 According to the invention, therefore, there is provided a method for the treatment of waste water containing dissolved nitrite ions prior to discharge thereof to the environment, which comprises adjusting the pH of the waste water to 2 to 5, treating the waste water with hydrogen peroxide so as to oxidise nitrite ions to nitrate ions, and then neutralising the resulting aqueous solution.

The method according to the invention is suitable for automatic operation and the oxidant and 25 oxidation products are non-polluting.

Reference will now be made to the accompanying drawings, in which:

Fig. 1 is a curve diagram indicating the relationship between an amount of a hydrogen peroxide solution added to aqueous solutions containing a nitrous acid radical whose pH has been adjusted to various levels and the levels of the oxidation-reduction potential;

30 Fig. 2 illustrates changes in the oxidation-reduction potential (ORP) resulting from the intermittent introduction of hydrogen peroxide as applied in this invention; and

Fig. 3 is a block circuit diagram of a voltage comparator P provided with various control units used in the invention.

The method of this invention for oxidizing a nitrous acid radical is based in principle on the 35 following reaction formula (1):



The inventors have studied the favorable conditions for effecting the above-mentioned reaction. As a result, it has been found that the reaction prominently varies with the pH value of the aqueous solutions containing a nitrous acid radical. Chemical analysis of the progress of oxidation of said nitrous 40 acid radical carried out with the pH value of the aqueous solutions varied to different levels indicates that where the pH value increases over a level of 6, the oxidation of said nitrous acid radical little proceeds. Where the aqueous solutions are very much reduced in the pH value to be highly acidified, then there arises the following reaction (2) in addition to the aforesaid reaction (1):



As a result, a harmful NO_2 gas is released into the atmosphere, failing to fully attain the intended object of treating the nitrous acid radical. However, the evolution of said NO_2 gas can be suppressed by controlling the pH value of an aqueous solution containing a nitrous acid radical (hereinafter referred to as "an aqueous solution being treated"). It is necessary to adjust the pH value of an aqueous solution 50 being treated to a higher level than 2 in order to minimize the evolution of NO_2 gas during the oxidation of the nitrous acid radical by hydrogen peroxide to such a level as raises no practical problems. It is therefore advised to oxidize the nitrous acid radical of an aqueous solution being treated with the pH value controlled to a level of 2 to 5, or more preferably to a level of 3 to 4.

An inorganic acid such as sulfuric acid or hydrochloric acid can be used to adjust the pH value of 55 an aqueous solution being treated within a range of 2 to 5. After the nitrous acid radical is oxidized by hydrogen peroxide, it is necessary to discharge the treated waste water with the pH value thereof adjusted to 7 by neutralization with alkali. In this case, inorganic alkali such as sodium hydroxide or sodium carbonate is used.

Where the treating method of this invention is applied, it is necessary to apply hydrogen peroxide

in an amount sufficient out not excessing for oxidation of all the nitrous acid radicals contained in an aqueous solution being treated into a nitric acid radical. The reason for this is that if hydrogen peroxide is applied in excess, the hydrogen peroxide itself conversely increases the COD value of said aqueous solution. For application of a proper amount of hydrogen peroxide, it is necessary to carry out in advance the quantitative analysis by potassium permanganate of an aqueous solution being treated in order to determine an amount of hydrogen peroxide to be used and, after oxidation of the nitrous acid radical too, examine the residue of the nitrous acid radical by the same quantitative analysis. Further, as need arises, the COD value of an aqueous solution thus treated has to be minutely controlled to minimize the COD value.

Since the above-mentioned operation involves complicated processes, the inventors have studied to develop an instrument allowing for the continuous measurement of necessary data. As a result, it has been found that the oxidation-reduction potentiometer is adapted to attain this object.

Fig. 1 shows changes in the oxidation-reduction potential of an aqueous solution being treated whose pH value has been set at various levels, when hydrogen peroxide is added to said aqueous solution. The oxidation-reduction potentiometer used was the type whose reference electrode was made of silver chloride and whose metal electrode was formed of platinum. Hydrogen peroxide aqueous solution with a concentration of 5.8 mol/l was added to 63 ml of a solution of sodium nitrite having a concentration of 0.165 mol/l. Where an aqueous solution being treated had a higher pH value than 6, the reaction of the formula (1) did not take place. First addition of a small amount of hydrogen peroxide caused only a slight change in the potential of the aqueous solution. Succeding addition of hydrogen peroxide kept the potential still at the same level. Where, however, hydrogen peroxide was added to the aqueous solution with pH set at a lower level than 6, then the potential of said aqueous solution rose higher, as hydrogen peroxide was added, and sharply dropped when reaction between the nitrous acid radical of the aqueous solution and hydrogen peroxide was completed, thereby indicating a distinct end point of reaction. In the above-mentioned test, with a pH lower than 6, reaction between the nitrous acid radical of the aqueous solution and hydrogen peroxide showed a distinct end point, though the potential of acid aqueous solutions varied with the initial pH value thereof. During the reaction, changes in the potential of the aqueous solutions were affected by ions present in said solutions. In all cases, however, the potential of the aqueous solutions indicated a sharp drop when the reaction was brought to an end. Changes in the potential at the end of the reaction are affected by the type of the metal electrode used. It is preferred to apply such a metal electrode as platinum or platinum black in the surface of which the reaction proceeds fully fast.

Based in the above-mentioned facts, the inventors have studied a method of automatically treating plant waste water containing a nitrous acid radical, and developed a new automatic system for said treatment.

Where plant waste water containing a nitrous acid radical is oxidized on an industrial scale in accordance with the method of this invention, then the plant waste water is put in a large tank with a stirrer, followed by the adjustment of the pH value of said waste water. A small amount of hydrogen peroxide is added to said waste water intermittently at a predetermined time interval. Fig. 2 shows changes in the potential of an aqueous solution containing a nitrous acid radical such as plant waste water when hydrogen peroxide was added thereto. During the periods A, B, C, D, E immediately after addition of hydrogen peroxide, the potential of the aqueous solution noticeably fluctuated. At points of time, a, b, c, d, e, a certain length of time after addition of hydrogen peroxide, the aqueous solution showed a stable potential. A length of time required for the fluctuation of the potential occurring after addition of hydrogen peroxide to disappear can be experimentally determined in advance with ease, though said time varies with, for example, the amount of the aqueous solution which is held in a tank.

The potentials of the aqueous solution at points of time a, b, c, d, progressively increase, and decrease the end point e of reaction between the nitrous acid radical of the aqueous solution and hydrogen peroxide. At this point of time, addition of hydrogen peroxide is stopped. However, it is difficult to trace the shifting of the pointer of an oxidation-reduction potentiometer by the eye and determine the end point of the reaction. Therefore, the inventors have developed an automatic waste water-treating method which is designed to utilize an electric signal coming from the oxidation-reduction potentiometer and stop the supply of hydrogen peroxide at the end point of the reaction.

There will now be described the sequential steps of the waste water-treating system embodying this invention by way of indicating the principle on which said system is based.

(1) Hydrogen peroxide is added intermittently in small predetermined amounts to an aqueous solution being treated. Measurement is made of the stable potential of said aqueous solution in a certain length of time after addition of hydrogen peroxide. The measured data is stored in a memory.

(2) Comparison is made between every two successive measurements of the potential to compute a variation, for example, a difference between the preceding and succeeding measurements of a quotient arrived at by dividing the preceding measurement by the succeeding measurement.

(3) Where the measured variation tends to increase, then hydrogen peroxide continues to be added.

(4) Where the measured variation tends to decrease, then the decreased variation is compared

with a preset value. If the absolute value of the variation is larger than said preset value, then addition of hydrogen peroxide is stopped.

Obviously, each charge of hydrogen peroxide should be so determined as not to result in an eventual rise in the COD value of the treated aqueous solution over the predetermined allowable level, even if one extra charge is given at the end point of the oxidation reaction of the nitrous acid radical.

There will now be described by reference to the block circuit diagram of a voltage comparator shown in Fig. 3, the arrangement and operation of an automatic waste water-treating method embodying this invention.

An oxidation-reduction potential (hereinafter referred to as "the ORP") measured by an oxidation-reduction potentiometer 4 is used as an input voltage to a voltage comparator P. This input voltage is amplified by an amplifier 5. When a measurement timer 6 issues a measurement-commencing instruction, the amplified voltage signal is converted into a digital signal by an analog-digital converter (A/D CONV) 7. The magnitudes of an ORP digital signals obtained at the respectively adjacent points of time, for example, a and b, b and c, c and d, d and e (Fig. 2) are compared by an up-down counter 8. A signal denoting the result of said comparison is conducted to a comparator 9, where the result of said comparison is further compared with the digitally expressed voltage level preset in a digital presetter 10. Where counts made by the up-down counter 8 indicate that the value measured at the preceding point of time is higher than that measured at the succeeding point of time (for example, the value measured at the point of time d is higher than that measured at the point of time e), namely, that a variation between the values measured at two adjacent points of time indicates a decrease; and a variation, for example, a difference between the preceding and succeeding measurements or a quotient arrived at by dividing the preceding measurement by the succeeding measurement is larger than a voltage level preset in the digital presetter 10, then a relay 11 is actuated to stop the subsequent addition of hydrogen peroxide. Where the above-mentioned difference is smaller than a voltage level preset in the digital presetter 10, then the relay 11 is not energized, allowing the intermittent addition of hydrogen peroxide to be continued. The digital presetter 10 is provided to prevent the occurrence of an erroneous automatic control due to the measurement errors of the measuring instruments used for the subject waste water-treating method. Where a difference between the potential levels measured at two adjacent points of time is so small as to fall within the range of the measurement errors of the instruments (caused, for example, by electric noises and impurities deposited on an ORP electrode set in the waste water being treated), then the relay 11 would be liable to make an erroneous operation, if the digital presetter 10 were not provided. Therefore, the digital presetter 10 causes the relay 11 to be energized only when a difference between two adjacent potential levels compared by the comparator 9 is larger than the potential preset in the digital presetter 10.

The required total quantity of hydrogen peroxide may be intermittently added in the predetermined equal small amounts. To shorten a length of time required for addition of estimated total quantity of hydrogen peroxide, however, it is possible to add initially the greater portion of the total quantity of hydrogen peroxide and thereafter intermittently add the remainder in the predetermined small amounts.

With the automatic waste water-treating method of this invention, the ORP value is converted into a digital signal and the operation of the subject apparatus is controlled in accordance with the digitally expressed ORP value. The reason for this is that this arrangement can control the operation of said apparatus easily and with high precision. Obviously, the subject apparatus can be operated with the ORP value expressed in the analog form instead of converting said value into the digital form.

As described above, the system of this invention can automatically treat waste water containing a nitrous acid radical substantially to the full with the precision of treatment unaffected by the skill of individual operators, thus offering prominent industrial advantages.

This invention will be more fully understood by reference to the examples which follow.

Example 1

Insulation rubber layer of a cable was vulcanized, using a molten salt consisting of a mixture of 7% NaNO_3 , 40% NaNO_2 and 53% KNO_3 as a heating medium. The molten salt settled on the surface of the rubber covering was washed off with water. A sample of 1 ml was precisely weighed from waste water of 5 m^3 which had been repeatedly used in the above-mentioned washing and thus containing a high concentration of the molten salt. The precisely weighed sample was diluted with distilled water to 100 ml. 10% sulfuric acid was added to the diluted solution to set its pH value at 3. Titration was made by 1/40 N aqueous solution of potassium permanganate. 14.3 ml of said aqueous solution was required for titration. The result of the titration showed that the above-mentioned sample solution contained 12.7 g/l (about 12560 ppm) of sodium nitrite. It was inferred from the result of said titration that the waste water of 5 m^3 contained 63.6 kg of dissolved sodium nitrite, or 2860 ppm as measured on the basis of the COD value.

It was found that 31.3 kg of hydrogen peroxide in terms of 100% H_2O_2 was required for complete treatment of the waste water assuming that the oxidation reaction expressed by the formula (1) took place.

About 10% sulfuric acid was added while being to the 5 m^3 waste water to set its pH value at 3.

Thereafter, commercially available 35% hydrogen peroxide solution for industrial use (where H_2O_2 content was chemically analyzed to be 34.99%) was slowly added, while the waste water was stirred. A sample was taken from the waste water after further stirring of two minutes. The sample was quickly titrated by an aqueous solution of 1/40 N potassium permanganate. The titration showed that the sample contained 0.022 g/l (22 ppm) of nitrous acid radical in terms of sodium nitrite. This content of a nitrous acid radical was equivalent to 5 ppm as a COD value, proving that the waste water was fully treated with hydrogen peroxide. Thereafter, the waste water was adjusted in pH value at about 7 by addition of 10% aqueous solution of sodium hydroxide and then was thrown away.

Example 2.

5 m³ of the same untreated waste water as in Example 1 was put in a tank provided with a stirrer. The pH value of the waste water was set at 3 by about 10% aqueous solution of hydrochloric acid. The waste water was treated by the automatic treating system of this invention shown in Fig. 3. Commercially available 35% hydrogen peroxide solution for industrial use (whose H_2O_2 content was chemically analyzed to be 34.99%) was intermittently added to the waste water under the following conditions:

Amount of each charge	200 milliliters
Time used per addition	16 seconds
Time interval of intermittent addition	about 110 seconds

The potential of the waste water was measured 5 seconds after the above-mentioned intermittent addition of hydrogen peroxide. The voltage of the digital presetter 10 was set at 0.05 mb. After the addition of hydrogen peroxide was automatically stopped, the same chemical analysis as in Example 1 was conducted. The chemical analysis showed that the waste water thus treated contained 0.031 g/l (31 ppm) of a nitrous acid radical in terms of sodium nitrite. This content was equivalent to 7 ppm as a COD value, providing that the waste water had been fully treated. Thereafter, the waste water was adjusted in pH value at about 7 by addition of about 10% aqueous solution of sodium hydroxide, and then was thrown away.

Claims

1. A method for the treatment of waste water containing dissolved nitrite ions prior to discharge thereof to the environment, which comprises adjusting the pH of the waste water to 2 to 5, treating the waste water with hydrogen peroxide so as to oxidise nitrite ions to nitrate ions, and then neutralising the resulting aqueous solution.
2. A method according to claim 1, in which the waste water is adjusted to a pH of 3 to 4.
3. A method according to claim 1 or 2, in which the pH adjustment is effected by adding sulphuric acid, hydrochloric acid or nitric acid to the waste water.
4. A method according to any of claims 1 to 3, in which the end-point of the oxidation of nitrite ions to nitrate ions is determined using an oxidation-reduction potentiometer.
5. A method according to any of claims 1 to 3, in which the hydrogen peroxide is added to the waste water intermittently in successive amounts, each of which is insufficient, by itself, to oxidise all the nitrite ions initially present to nitrate ions, the oxidation-reduction potential of the thus treated aqueous solution being measured when said potential is in a stable state after each charge of hydrogen peroxide, the addition of hydrogen peroxide being stopped when the variation between successive oxidation-reduction potential measurements indicates a decrease in said potential.
6. A method according to claim 5, in which the addition of hydrogen peroxide is stopped when the variation between successive oxidation-reduction potential measurements is larger than a predetermined amount.
7. A method according to any of claims 1 to 6, in which the oxidation-reduction potential of the nitrite-ion-containing waste water is determined using an oxidation-reduction potentiometer, the thus determined potential is amplified, and when a measurement timer issues a measurement-commencing instruction after addition of successive amounts of hydrogen peroxide, the measured amplified voltage is converted into a digital signal by an analog-digital converter, the digital data is stored in an up-down counter, the variation between the digitally expressed oxidation-reduction potentials measured at the respective adjacent points of time is computed in said up-down counter, and the addition of hydrogen peroxide is stopped when said variation indicates a decrease in the oxidation-reduction potential.
8. A method according to claim 7, wherein a comparator compares the variation between the oxidation-reduction potentials measured after successive additions of hydrogen peroxide which indicates a decrease in said potential with a predetermined amount preset in a digital presetter; and when said variation is larger than said predetermined amount, a relay is energized to stop the addition of hydrogen peroxide.
9. A method of treating waste water, substantially as hereinbefore described in Example 1 or 2.

10. A method of treating waste water substantially as described herein with reference to Figure 3 of the accompanying drawings.

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